

DEPTH PROFILE STUDIES OF CATALYST/ LIQUEFIED COAL RESIDUES

J.Y. Kim, P.J. Reucroft and M. Taghei
Department of Materials Science & Engineering,
University of Kentucky, Lexington, KY 40506

V.R. Pradhan and I. Wender
Chemical Petroleum Engineering Department,
University of Pittsburgh, Pittsburgh, PA 15261

INTRODUCTION

Iron based catalysts with a high specific surface area and fine particulate size can be utilized at small concentrations to achieve better performance in terms of overall coal conversion and selectivity to lighter products (oils) in direct coal liquefaction.¹ Since the surfaces of catalysts are the primary site of catalytic activity, efforts have been directed to characterizing catalyst surfaces in coal liquefaction environments. X-ray photoelectron spectroscopy (XPS) has been used to study the iron-based catalyst impregnated liquefied Blind Canyon coal residue samples at different liquefaction processing times (17, 30 and 60 minutes). It was shown that the concentration of elements at the outermost surface layer of samples measured by XPS is similar to that determined in the bulk by chemical analysis but differs from the bulk composition in some important respects.² In order to more carefully delineate the differences in the distribution of the elements and chemical changes between the surface and the bulk, the samples have been further analyzed by combining Ar⁺ ion sputtering with XPS measurements. Special emphasis has been focused on the surface to bulk distributions of the catalytic elements iron and sulfur. The Fe peaks were not observed for most samples unless Ar⁺ ion sputtering was carried out for long times. The S/Fe (catalyst element) ratio, which was initially greater than 1, decreased consistently to less than 1 as time of Ar⁺ ion sputtering was increased.

EXPERIMENTAL

Three different liquefaction processing times (17, 30 and 60 min.) of iron-based catalyst impregnated Blind Canyon coal samples were investigated in the surface characterization studies. Liquefaction conversion was carried out at 400 °C with tetralin as solvent (1:1.5 coal/solvent ratio) after adding Fe₂O₃/SO₄²⁻, so that the proportion of Fe was 5% by weight. Dimethyl disulfide was also added in amounts equivalent to Fe to promote sulfidation of the catalyst. The catalyst impregnated liquefied Blind Canyon coal residues were removed in liquid-like form after 17, 30 and 60 minutes and kept in a vacuum oven at 65 °C for 2 days to remove volatile material in the residue without exposing to an air atmosphere. The liquid-like samples were then mounted on the spectrometer probe tip by means of double-sided adhesive insulating tape. After heat treating at 65°C for 10 hours in a pretreatment chamber to remove remaining volatile materials from the coal residues, the samples were inserted into an ultrahigh vacuum chamber for surface analysis. To exclude the possibility of recording contaminants associated with the tape, the tape was also analyzed separately. It was found that the constituents of tape were not detected by XPS, and that the photoionization signals were characteristic of the samples alone.

The samples were examined by XPS employing a Kratos XSAM 800 spectrometer using Mg K α ($h\nu = 1253.6$ eV) radiation. The spectrometer was run in Fixed Analyzer Transmission (FAT) mode at pass energy of 11 kV and 13 mA. Under these conditions, the FWHM of Ag (3d $_{5/2}$) peak is ≈ 1.0 eV. The system pressure never exceeded 3×10^{-8} torr during spectra acquisition. In situ Ar $^+$ ion sputtering of the residue samples was carried out using a differentially pumped and computer controlled 3M mini-beam ion gun. The ion beam was adjusted so that edge effects were minimized. Incident ion energy used was 3.5 kV and the sample currents were kept around 30 μ A (estimated etching rate was approximately 25 Angstroms/min, as determined from a SiO $_2$ standard film). The pressure in the main chamber was kept below 4×10^{-6} torr during ion sputtering. After ion sputtering, a consistent increase in the FWHM for all elements was found with increasing ion dose. No compensation was made for charging of the samples.

RESULTS AND DISCUSSION

The initially recorded XPS spectra showed a distinct peak for each of the major elements, carbon, oxygen, and silicon, as well as the minor components, sulfur and nitrogen in each sample. Binding energies of these elements showed the expected values for the most stable oxidation state and were similar to those reported previously.² However, Fe was not observed initially in the surface regions of the liquefied coal residue particles. A relatively high oxygen concentration was determined initially at the surface by XPS before sputtering, but a sharp drop in oxygen concentration was subsequently observed. This surface enrichment of oxygen can be ascribed to air oxidation and the oxidized layer thickness was estimated to be 50-60 nm.

Two peak components were initially observed in the case of the surface sulfur XPS signal. The peak at 168 eV, can be ascribed to oxidized sulfur, i.e., organic plus inorganic (sulfate), while the other at 163 eV corresponded to inorganic sulfide plus the usual organic sulfur forms present in coal (thiophene, sulfides, mercaptans). As sputtering increased, the sulfate peak decreased and finally disappeared, while the sulfide peak showed an increase in intensity. This observation is in agreement with the decrease of oxygen concentration which was observed as the sputtering increased. These results are similar to those reported previously.²

The Fe peaks were not observed initially for most samples unless ion sputtering was carried out for at least 30 minutes. As the liquefaction reaction time increased from 17 to 60 min, sputtering time had to be further increased in order to observe the Fe peaks. Catalytic elements such as iron and sulfur showed a systematic trend towards higher concentrations of each sample after 30 min Ar $^+$ sputtering. The results are shown in Figures 1, 2, and 3. From these results, it can be concluded that the iron catalyst particles are well encapsulated in either oxide layers or within other organic materials from the coal residues.

The S/Fe (catalyst element) ratio, which was initially greater than 1, decreased consistently to less than 1 as time of Ar $^+$ ion sputtering was increased (Tables 1, 2 and 3). This is also shown in Figures 1, 2 and 3 for liquefaction times of 17, 30 and 60 minutes, respectively. EXAFS and Mossbauer studies have shown that under the liquefaction conditions that were employed i.e., after adding dimethyl disulfide to the catalyst/coal residue mixtures, the iron catalyst is converted to iron sulfide (pyrrhotite) within a few minutes of starting the reaction.³ Further analysis is currently underway.

SUMMARY AND CONCLUSIONS

Surface analysis combined with depth profiling shows that the sulfur/iron stoichiometry varies in iron catalyst/liquefied coal residues that have been extracted from coal liquefaction environments. The catalyst elements become increasingly more encapsulated in the carbonaceous material as the processing time increases. The S/Fe atomic ratio approaches 0.7 to 0.9 inside the coal residue particles.

ACKNOWLEDGEMENT

We gratefully acknowledge financial support from the Consortium for Fossil Fuel Liquefaction Science, University of Kentucky under Dept. of Energy Contract No. DE-FC22-92 PC 90029. We also thank Dr. G.P. Huffman for his interest in this work.

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Table 1. XPS Catalyst Element Depth Profile for Ar⁺ Sputtered 17 min Liquefied Coal Residues (atomic %)

	0 min	10 min	20 min	30 min	40 min	50 min	60 min
S	0.38	0.48	0.76	0.50	0.58	0.73	0.89
Fe	-	-	-	0.40	0.73	0.89	1.24
S/Fe	-	-	-	1.25	0.79	0.82	0.72

Table 2. XPS Catalyst Element Depth Profile for Ar⁺ Sputtered 30 min Liquefied Coal Residues (atomic %)

	0 min	10 min	20 min	30 min	40 min	50 min	60 min
S	0.25	0.23	0.34	0.43	0.51	0.72	0.97
Fe	-	-	-	0.20	0.45	0.69	1.12
S/Fe	-	-	-	2.15	1.13	1.04	0.87

Table 3. XPS Catalyst Element Depth Profile for Ar⁺ Sputtered 60 min Liquefied Coal Residues (atomic %)

	0 min	10 min	20 min	30 min	40 min	50 min	60 min
S	0.62	0.53	0.42	0.38	0.37	0.62	0.63
Fe	-	-	-	0.17	0.23	0.52	0.74
S/Fe	-	-	-	2.24	1.61	1.19	0.85

Figure 1. Depth Profile of Elements for 17 min. Coal Liquefaction Residue

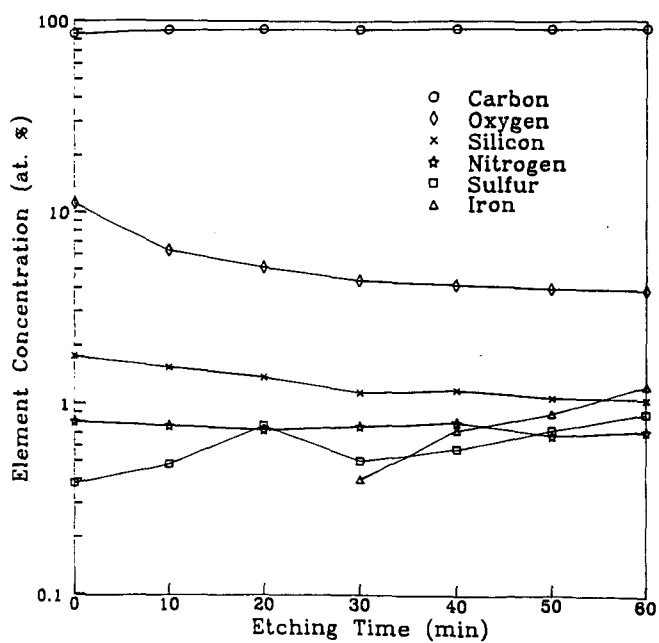


Figure 2. Depth Profile of Elements for 30 min. Coal Liquefaction Residue

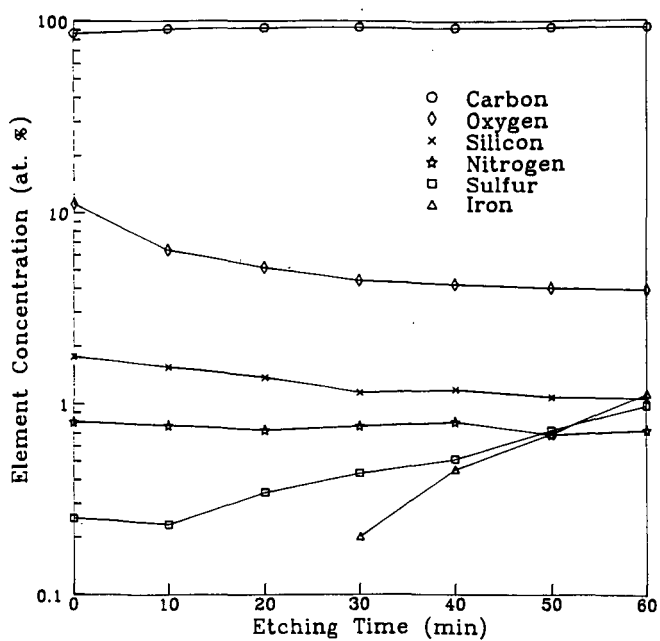


Figure 3. Depth Profile of Elements for 60 min. Coal Liquefaction Residue

